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The Use of Commercial Non-Hazardous Air Pollutant Monomers to Optimize the Properties of Fatty Acid-Based Resins

by John J. La Scala, Priya Kamath, Anita Sahu, Giuseppe R. Palmese, and James M. Sands

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14. ABSTRACT

Vinyl ester (VE) resins are used to make polymer matrix composites in military and commercial applications because of their good properties, low weight, and low cost. These resins typically contain high concentrations of reactive diluents, such as styrene, to allow these resins to be molded using resin transfer molding and other inexpensive liquid molding techniques. Fatty acid vinyl ester (FAVE) resins, which use fatty acid monomers to replace some of the styrene content in VE resins, were developed to provide composites with lower hazardous air pollutant (HAP) emissions. The properties of FAVE resins can be improved, and further reduction in styrene emissions can occur through replacement of some the fatty acid monomer and/or styrene with a non-HAP petroleum derived monomer. Mono- and di-functional non-HAP petroleum monomers were blended into fatty acid vinyl ester resins to decrease styrene content, reduce viscosity, and improve polymer properties. It was found that cyclohexyl methacrylate (CHMA) was the most effective reactive diluent in replacing methacrylated lauric acid (MLau) because it effectively reduced viscosity and improved thermal and mechanical properties. However, replacing styrene with CHMA resulted in a viscosity increase and polymer property decrease. All petroleum di-functional monomers were effective in reducing the viscosity through replacement of the MLau fraction. However, only hexanediol dimethacrylate (HDDMA) allowed further reduction in styrene content with little effect on viscosity and improved or similar polymer properties. Ignoring economics, using a small percent HDDMA to replace styrene or MLau is optimum and would result in improved resin and polymer performance. CHMA can be used to effectively reduce the MLau content in the formulations with improved resin and polymer performance, but would not allow for further reduction in styrene content. All of the other monomers investigated can result in some property improvements, but simultaneously result in other property reduction.

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1. Introduction

Vinyl ester (VE) resins are used to make polymer matrix composites in military and commercial applications because of their good properties, low weight, and low cost. These resins typically contain high concentrations of reactive diluents, such as styrene, to allow these resins to be molded using resin transfer molding and other inexpensive liquid molding techniques. Because styrene is a hazardous air pollutant (HAP) and a volatile organic compound (VOC), the Federal Environmental Protection Agency of the United States of America introduced legislation to limit styrene emissions from composite manufacturing (*1*).

Unfortunately, decreasing the styrene content in VE resins does not offer an acceptable solution to this problem. As the styrene content is reduced, the fracture toughness decreases and the resin viscosity increases, making it difficult to use inexpensive molding techniques (*2*, *3*). For example, Dow Derakane 441-400 uses 27% less styrene than Derakane 411-C50 (*4*, *5*), but has less than half the fracture toughness (*6*, *7*).

Various monomers with volatilities lower than that of styrene have been used as styrene replacements, such as vinyl toluene (8). First of all, these styrene replacements still produce significant VOC emissions, and are therefore still regulated by the EPA (*1*). In addition, few monomers yield resins with properties comparable to styrene based resins, and even fewer can match the low cost of styrene.

Recently, fatty acid-based monomers have been used in VE resins to reduce the styrene content (*9*, *10*). Fatty acid monomers are excellent alternatives to styrene because of their low cost and low volatility. Fatty acids are renewable resources because they are derived from plant oils. Therefore, not only would the use of fatty acids in liquid molding resins reduce VOC emissions, thereby reducing health and environmental risks, but it also would promote global sustainability. On the other hand, fatty acid monomers tend to lower the glass transition temperature (T_g) of the polymer and increase the resin viscosity. High viscosities can cause problems with fiber wetting, voids may occur in the part and the time required for injection increases (*2*, *3*). As the temperature increases, polymers become softer. As T_g is approached, the modulus decreases drastically with temperature until it is a rubber at high temperature. Resins with high fatty acid contents and low styrene contents (<20 weight-percent) would require long infusion times and would produce polymers useable only at relatively low operating temperatures. A high modulus and high T_g are necessary for materials to be used in more demanding applications such as boat hulls and automobile parts.

Further reductions in styrene content would be useful in meeting EPA regulations. One way of doing this is to replace more of the styrene in fatty acid-based VE with low volatility non-HAP petroleum monomers. These petroleum monomers have methacrylate groups enabling them to

free-radically polymerize with vinyl ester. Unlike vinyl toluene, the petroleum monomers used in this work have volatilities that are orders of magnitude lower than that of styrene, thus severely reducing VOC and HAP emissions.

Resins were formulated using low volatility petroleum comonomers and fatty acid monomers to determine whether resin and polymer properties can be maintained while having low styrene content. These low VOC formulations should have viscosities less than 500 cP, which is typically considered the maximum for liquid molding operations (2, 3). In liquid molding, fibers (glass, carbon, flax, etc.) are placed in a mold and the liquid monomeric resin is pulled into the mold using vacuum. Low viscosities are necessary to ensure good fiber wetting and low void contents. High polymer properties, specifically T_g and modulus are necessary to increase the operating range of these materials. Commercial vinyl ester systems have T_g of ~120ºC and modulus of ~ 3 GPa (4, 5, 6, 10). Finally, styrene contents of no more than 33 weight-percent are desired because of the federal NESHAPs. However, states are allowed to make these emissions standards more strict, which will likely be the case in California and other states with large metropolitan centers. Therefore, it is desired to make resins with the lowest possible styrene contents. Since we have made successful fatty acid-based vinyl esters with 20 weight-percent styrene, the low VOC/HAP petroleum comonomers were added to those resin formulations in an effort to lower the styrene content in the resins or make polymers with better properties using 20 weight-percent styrene.

2. Experimental

2.1 Fatty Acid Monomer Preparation

A number of synthetic procedures have been established for making fatty acid-based monomers to be used as the reactive diluent in VE resins (9, 10). Figure 1 depicts the synthetic route used to form methacrylated lauric acid (MLau). The carboxylic acid of fatty acids undergoes a simple addition reaction with the epoxide group of glycidyl methacrylate (GM) (Aldrich, Milwaukee, WI) to form a single product. Stoichiometric quantities of the reactants were mixed together and reacted at 70 °C for 2.5 hr using 1 weight-percent AMC-2 catalyst. FTIR and ^{1}H-NMR (250.13 MHz, spectral window of ± 2000 Hz, 0.427 Hz/pt digital resolution, 16 scans at 293 K, 90° pulse width) with a Bruker (Billerica, MA) AC250 Spectrometer showed that methacrylation of the fatty acids went to completion. Each methacrylated fatty acid (MFA) contains one terminal polymerizable unsaturation site per molecule. In this way, the fatty acid monomers act as chain extenders, analogous to styrene, in VE resins. MLau is a fairly long hydrocarbon, with a length of 20 atoms. Other fatty acids have been used to prepare MFA monomers; however, MLau results in better resin and polymer properties than longer fatty acids (e.g., stearic acid) and is considerably less expensive than shorter fatty acids (hexanoic acid).
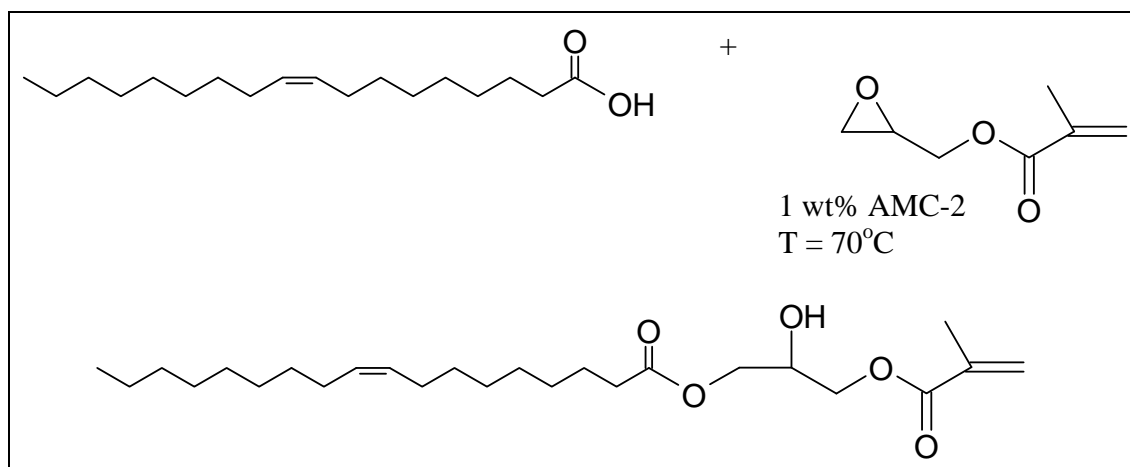
Figure 1. The reaction of glycidyl methacrylate and lauric acid to produce the MLau monomer.

2.2 Resin Formulation

Resins were prepared using 45, 55, and 65 weight-percent VE monomers. Vinyl esters are dimethacrylates of diglycidyl ether of bisphenol A (DGEBA) (figure 2) (*2*). CN151 (Sartomer) is a low molecular weight vinyl ester. Studies have shown that it has similar properties relative to VE 828 (*11*). MLau and styrene (Aldrich 99%) were added in the amount of 10–20 weight-percent. Two types of non-HAP petroleum comonomers were used: mono-functional and di-functional. The mono-functional monomers contained a single free-radically polymerizable group while the di-functional monomers contained two free-radically polymerizable groups, one on each end of the molecule. The mono-functional monomers were used with resins containing 65 and 55 weight-percent VE monomer. The di-functional monomers were used with resins containing 55 and 45 weight-percent VE monomer. Therefore, the di-functional monomers were not only used to help reduce the styrene content in the resin, but were also used to reduce the VE content.

The di-functional petroleum monomers (cross-linkers) PEG 600 dimethacrylate (SR252), PEG 200 diacrylate (SR259), 1,6-hexanediol dimethacrylate (SR239 or HDDMA), and ethoxylated (10) bisphenol A dimethacrylate (SR480) were all supplied by Sartomer (figure 2). The mono-functional petroleum monomers (reactive diluents) methoxy PEG 350 methacrylate (CD550) and ethoxy (4) nonyl phenol methacrylate (CD612) and were supplied by Sartomer and cyclohexyl methacrylate (CHMA) was purchased from Aldrich (figure 3). The properties of these monomers as well as the MLau, styrene, and vinyl ester are listed in table 1.

Four component resin blends were prepared by mixing VE, MLau, styrene and non-HAP petroleum monomers. First, the CN151 was heated for 10 min at 70 °C for easy pouring. After heating CN151, 9–11 g were carefully poured into a 20-mL scintillation vial. Based on this vinyl ester content, the amounts of other monomers were calculated according to their particular formulation. Di-functional monomers were added after the vinyl ester. After the di-functional monomer was added, the MLau was poured into the vial. When mono-functional petroleum
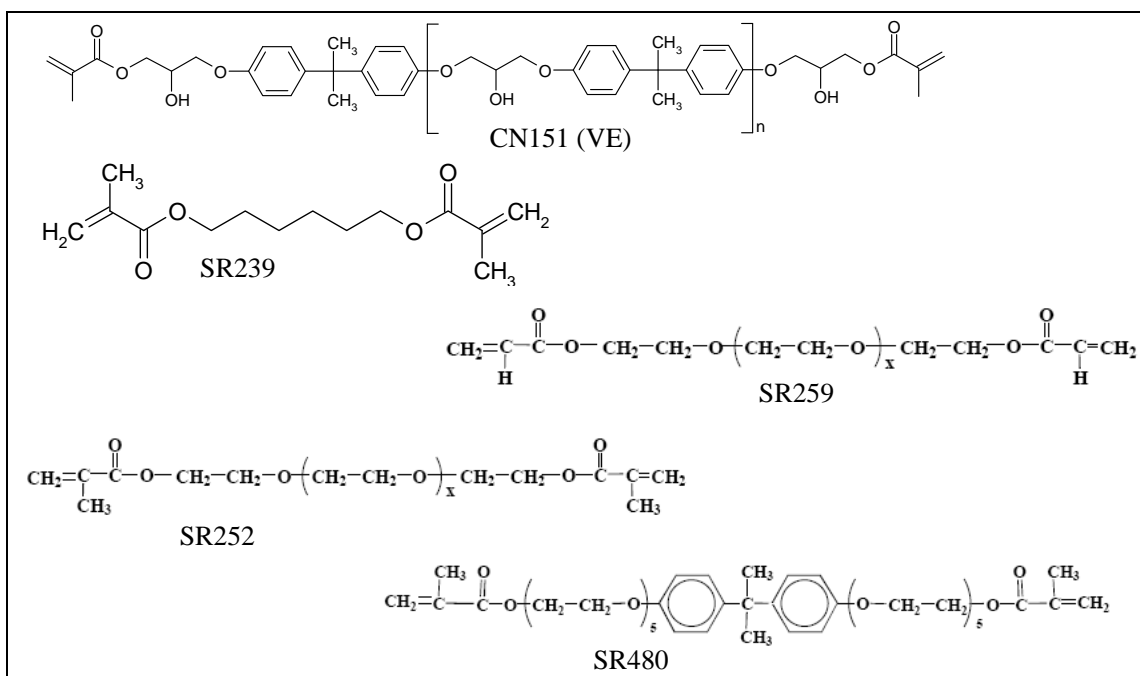
Figure 2. Molecular structures of the cross-linking agents used in this work.
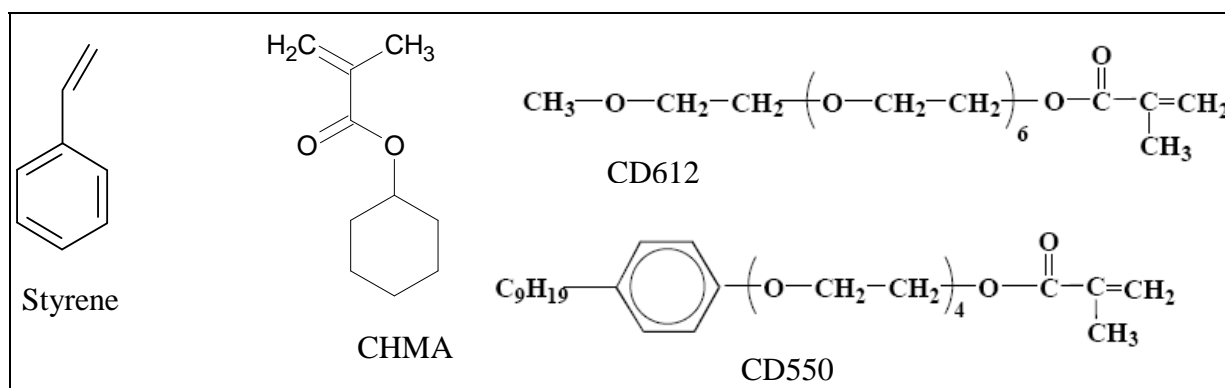
Figure 3. Molecular structures of the petroleum reactive diluents used in this work.

monomers were used, MLau was added to the vial after the vinyl ester followed by the mono-functional monomer. The styrene was added last because of its hazardous properties. After all of the solutions were added to the vial, it was heated at 70 °C for 5 min and then manually stirred with a glass stirring rod to dissolve the components. The clarity of the solution was noted. Ternary blends of VE, MLau, and styrene were prepared for comparison purposes to the four-component blends.

Table 1. The viscosity at 25 °C of the monomers used in this work and T_g homopolymers (*12*).

Monomer	Label	Polymerizable Groups	Viscosity (cP)	T_g (°C)	Molecular Weight (g/mol)
Styrene	Sty	1	0.7	100	104
Cyclohexyl methacrylate	CHMA	1	2.5	NA	—
Methoxy PEG (350) methacrylate	CD550	1	19	–62	494
MLau	—	1	65 ± 4	–30	342
Ethoxy (4) nonyl phenol methacrylate	CD612	1	79	NA	464
1, 6-hexanediol dimethacrylate	SR239	2	8	NA	254
PEG (200) diacrylate	SR259	2	25	NA	302
PEG (600) dimethacrylate	SR252	2	67	NA	770
Ethoxylated (10) bisphenol dimethacrylate	SR480	2	410	–1	808
Vinyl ester	CN151	2	$3.9*10^5 \pm 0.2*10^5$	160	560

Note: NA = not applicable.

2.3   Rheological Characterization

The rheological character of the resins was measured using a TA Instruments AR 2000 rheometer. The geometry used for all the samples was the 40-mL parallel steel plates. The gap distances for all samples were set to 1000 µm. A constant temperature was used for all samples, which was 21 °C. A shear rate of 1 to 100 inverse seconds was used in increments of three points per decade for 25 decades on a logarithmic scale in a steady state experiment. The TA data analysis program was used to analyze the results from the rheometer.

2.4   Cure of VE Resins

Cure conditions significantly affect the microstructure of vinyl ester resins, which in-turn affects the thermal and mechanical of the resulting polymers (*6*). For these reasons, cure conditions (temperature, sample thickness, and cure time) were kept constant for all samples, unless otherwise noted.

VE monomer and styrene were mixed in various ratios. Trigonox 239A, containing 45 weight-percent cumene hydroperoxide, was used to initiate free radical polymerization of the resin. Cobalt naphthanate (CoNap) was used to catalyze the polymerization at room temperature. The moles of cumene hydroperoxide used were one-hundredth the number of moles of vinyl functionality. A 4:1 weight ratio of Trigonox to CoNap was used. The resins were then poured into a mold and allowed to cure at room temperature (22 °C) overnight, followed by a 2-hr postcure at 120 °C. These cure conditions are typical for vinyl ester resins, and results in highly cured polymers with good polymer properties (*4*, *5*, *6*, *10*).

2.5   Thermomechanical Characterization

The thermomechanical properties of vinyl esters were measured using dynamic mechanical analysis (DMA). Rectangular samples with ~dimensions of $25 \times 9 \times 3$ mm were tested using a TA Instruments 2980 DMA in single cantilever geometry. The samples were tested at 1 Hz with a deflection of 15 µm while ramping the temperature from 30 to 200 °C at a rate of 2 °C/min. Three temperature ramp experiments were run for each sample. The first ramp usually completely post-cured the polymer, but another ramp was performed to insure this. The temperature at which the peak in the loss modulus occurred in the fully post-cured polymer was considered the glass transition temperature of the material (*13*).

The cross-link density of the neat resins was measured using DMA. The theory of rubber elasticity was used to calculate the molecular weight between cross-links, M_c:

$$M_c = \frac{3RT\rho}{E} \; . \tag{1}$$

Here E is the rubbery modulus, R is the universal gas constant, T is the absolute temperature and ρ is the sample density (*13*, *14*). The temperature T and rubbery modulus E are determined for the calculation of equation 1 at the temperature at which the rubbery modulus no longer decreased with temperature. The sample density ρ was taken as 1.1 g/cm^3 (a common value for the vinyl ester resins). The density divided by M_c is the cross-link density of the polymer.

3.   Results

3.1   Viscosity

3.1.1 Monomer Viscosity

Viscous forces in liquids are caused by physical and chemical interactions between molecules. Physical interactions, such as chain entanglements, dominate in polymeric melts (*15*, *16*). For example, as the molecular weight of epoxy monomers increases, the viscosity of the melt increases because of an increase in the entanglements and loss of degrees of freedom (*17*, *18*). Hydrogen bonding, acid-base interactions, and other such chemical interactions can also greatly affect the viscosity of a substance. As seen with triglyceride-based liquid molding resins, the viscosity of the resin increases exponentially due to increased hydrogen bonding as polar functional groups are added to the triglyceride (*19*).

The viscosity of the pure monomers were measured or found in the literature (table 1). Styrene had the lowest viscosity because of its low molecular weight and lack of polarity. Therefore, decreasing the styrene content while keeping the vinyl ester content constant should increase the resin viscosity. CHMA has a slightly higher viscosity than styrene because of its larger

molecular weight and possibly also because of the higher polarity of the methacrylate group. On the other hand, the viscosity of the vinyl ester is orders of magnitude higher than that of any of the other monomers because of its higher molecular weight, its rigid nature, and the hydrogen bonding resulting from its hydroxyl groups. Therefore, reducing the vinyl ester content should have the largest effect on the resin viscosity. SR480 had the next highest viscosity, as expected based on its high molecular weight, but has a lower viscosity than the CN151 because of its lower rigidity (polyethylene glycol groups) and its lack of polar hydroxyl groups. MLau had a relatively high viscosity because of its large molecular weight and the presence of the polar hydroxyl group. SR252 had a higher viscosity than SR259 likely because the higher molecular weight of SR252. The monofunctional and di-functional monomers have similar viscosities.

3.1.2 Viscosity of VE/MLau/Styrene Ternary Blends

The viscosity of VE/MLau/styrene was measured at 21 °C and was found to decrease exponentially with increasing styrene content for resins containing 55 weight-percent and 65 weight-percent VE 828 resin (figure 4). VE 828, like CN151, is also a bisphenol A VE cross-linker, but has slightly lower molecular weight giving the resulting resins a lower viscosity and the polymers a slightly higher T_g. Styrene contents of 10% or greater reduced the viscosity of VE resins to the acceptable range (<500 cP). Therefore, only low styrene contents are necessary, from a viscosity viewpoint.
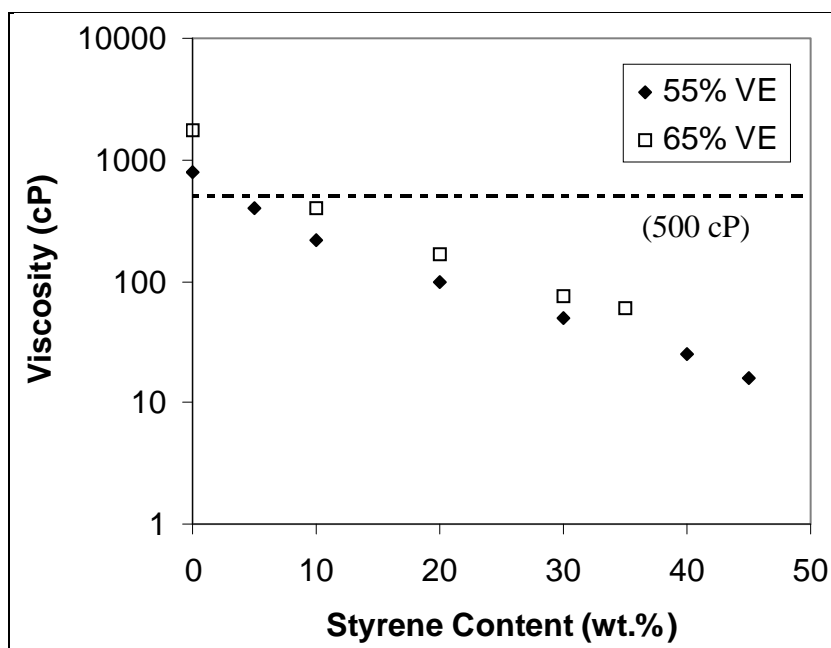
Figure 4. The viscosity of VE/MLau/styrene as a function of styrene content
in the resin for resins containing 55 and 65 weight-percent VE
828.

3.1.3 Viscosity of Low HAP, Four-Component Blends

Figure 5 shows the effect of resin formulation on the viscosity for resins composed with 65% CN151 and different percentages of mono-functional petroleum monomers and styrene. For example, it appears that the original ternary compound with 10% styrene had a viscosity of 1337 cP. Using the same components but with 25% styrene and less MLau had a lower viscosity (201 cP). Therefore, increasing the amount of styrene decreased the viscosity.
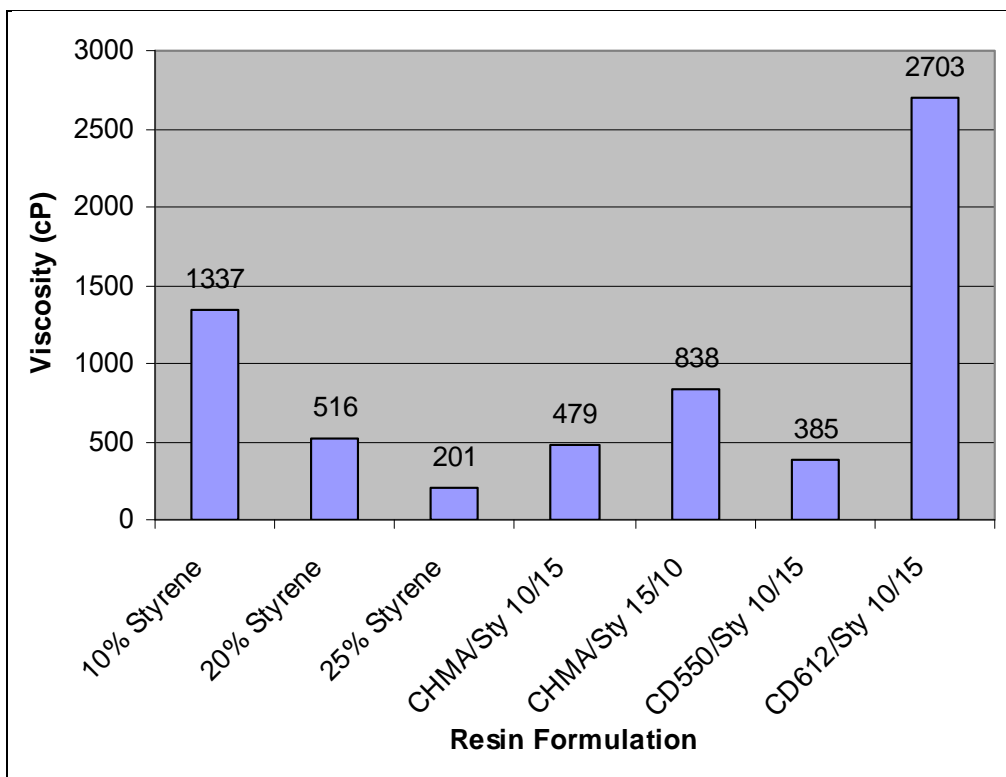
Figure 5. Viscosity as a function of mono-functional resin formulation for resins with 65% CN151. The resin content totals 100 parts, and the remaining resin content is the MLau.

All of the resins with the HAP-free petroleum monomers had a viscosity higher than 201 cP, which was expected based on the viscosities listed in table 1. No resin formulation containing CD612 had an acceptable viscosity of 500 cP or less including the one shown in table 2 (*2*). Furthermore, because the CD612 formulations had an even higher viscosity than CN151/MLau /Sty 65/25/10, this monomer would not be effective in replacing the MLau content to reduce resin viscosity. Again, this is expected because the viscosity of CD612 is higher than that of MLau (table 1). On the other hand, CD550 and CHMA were effective in reducing the resin viscosity through replacement of MLau, but increased the viscosity when replacing the styrene. The resins containing 55 weight-percent had lower viscosities relative the resins containing 65 weight-percent styrene. Otherwise, the trends were similar.

Table 2. Viscosity of resin formulations containing mono-functional petroleum monomers. Green shading indicates an acceptable viscosity below 500 cP, yellow shading indicates borderline viscosity, and red shading indicates unacceptable viscosity.

%VE (CN151) Weight-Percent	Petroleum Monomer	Petroleum Monomer (Weight-Percent)	MLau (Weight-Percent)	Styrene (Weight-Percent)	Viscosity (cP)
65	—	—	25	10	1340
65	—	—	20	15	830
65	—	—	15	20	520
65	—	—	10	25	200
65	CD550	10	10	15	480
65	CD612	10	10	15	2700
65	CHMA	10	15	10	840
65	CHMA	10	10	15	390
55	—	—	30	15	410
55	—	—	25	20	250
55	—	—	15	30	120
55	CD550	15	15	15	340
55	CD612	15	15	15	1800
55	CHMA	15	15	15	170

Figure 6 and table 3 shows the viscosity results for resins with 55% CN151 and di-functional monomers with 20% styrene, compared to the original ternary resin with no di-functional petroleum monomers added. All of the formulations produced acceptable viscosities below 500 cP. Furthermore, all petroleum monomers were successful in reducing the viscosity by replacing some of the MLau fraction. This was not expected for SR252 and SR480, which have similar and higher viscosities, respectively, compared with MLau. SR239 even managed to maintain the viscosity of the resin formulation when replacing the styrene fraction despite the higher viscosity of HDDMA. These results indicate that HDDMA, SR252, and SR480 allow the formulations of closer to an ideal solution than the ternary fatty acid resin blends. This may occur because their aliphatic nature may help shield the polar interactions between MLau monomers more effectively than VE and styrene.
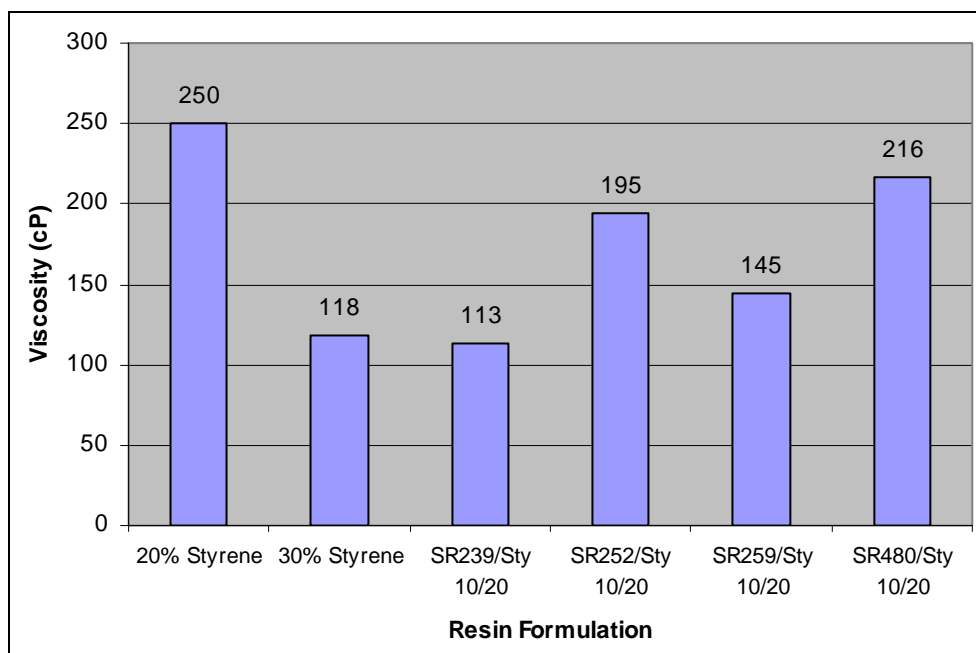
Figure 6. Viscosity as a function of di-functional resin formulation for resins with 55% CN151.

Table 3. Viscosity of resin formulations containing di-functional petroleum monomers. Green shading indicates an acceptable viscosity below 500 cP.

%VE (CN151) Weight-Percent	Petroleum Monomer	Petroleum Monomer Weight-Percent	MLau Weight-Percent	Styrene Weight-Percent	Viscosity (cP)
55	—	—	30	15	410
55	—	—	25	20	250
55	—	—	15	30	120
55	SR252	10	15	20	200
55	SR259	10	15	20	150
55	SR239	10	15	20	110
55	SR480	10	15	20	220
45	—	—	15	40	30
45	—	—	25	30	50
45	—	—	35	20	80
45	SR252	20	15	20	100
45	SR259	20	15	20	70
45	SR239	20	15	20	70
45	SR480	20	15	20	130

3.2 Polymer Properties

3.2.1 Dynamic Mechanical Properties of VE/MLau/Styrene Ternaary Blends

The DMA character of these resins improved as the styrene content increased (figure 7). Figures 8 and 9 show that both the modulus and T_g improved with increasing styrene content for resins using methacrylated oleic acid (MOA) and VE 828. These results show that 15% styrene is sufficient to obtain an acceptable modulus and T_g. Furthermore, at this styrene content, the resin viscosity is well within the acceptable window. When DMA is run at 2 °C/min ramp rates, the measured T_g values were at least 5 °C lower than for a ramp rate of 5 °C/min.

3.2.2 Dynamic Mechanical Properties of Low HAP, Four-Component Blends

Typical dynamic mechanical analysis plots are shown in figure 10. The storage modulus decreased with temperature. The loss modulus went through a maximum as a function of temperature. Figure 10 shows that the CHMA sample had a higher modulus and T_g than the CD-550 sample, and thus could be used at higher operating temperatures. Overall, the DMA plots (figure 10) are similar to VE/MLau/Styrene ternary blends (figure 7).
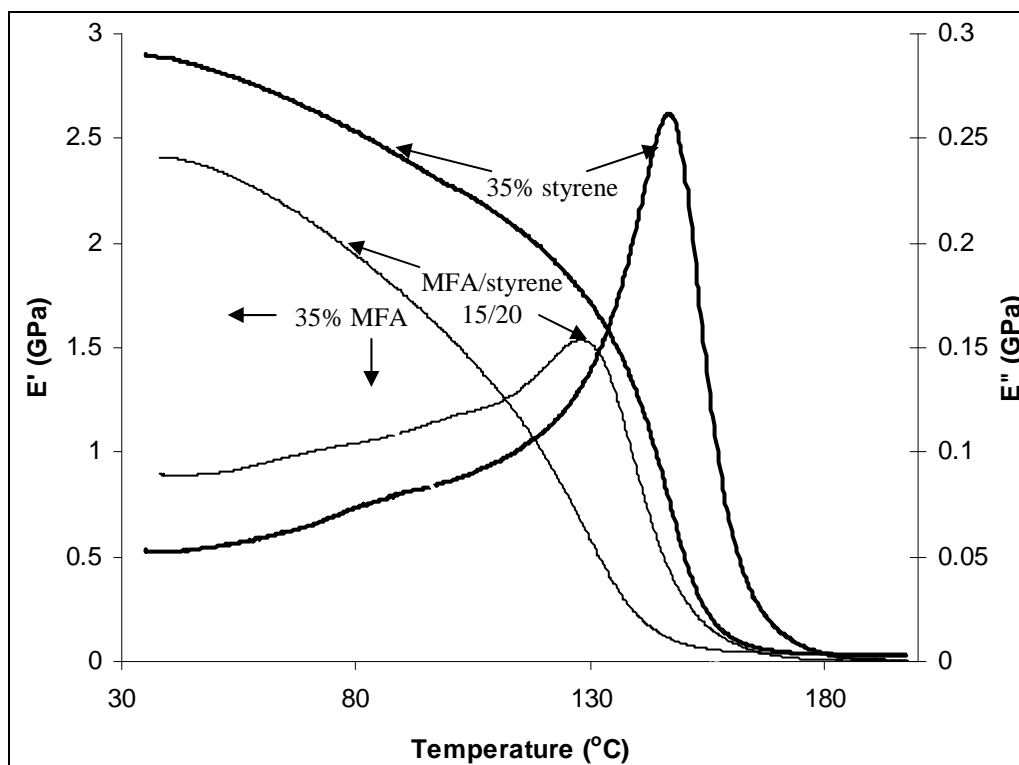

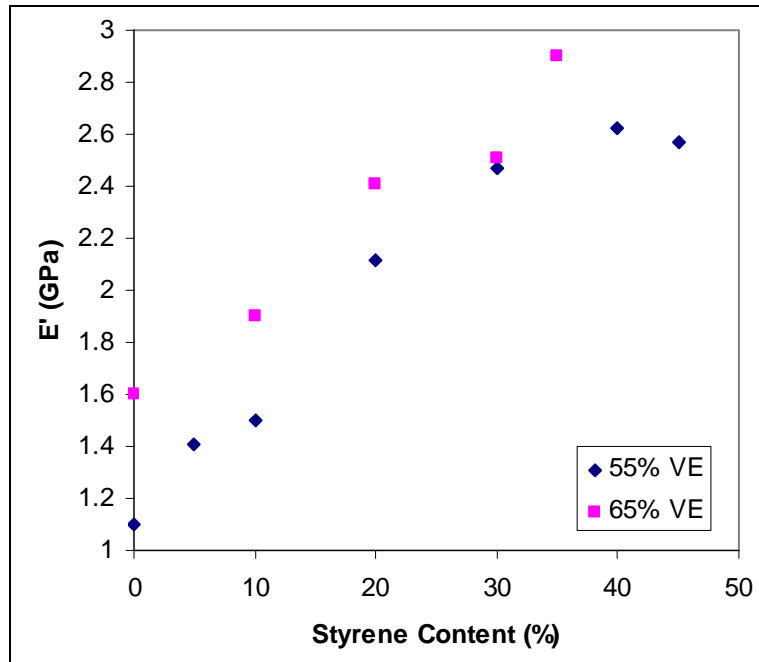Figure 7. DMA behavior of VE/MOA/styrene with 65 weight-percent VE 828.

Figure 8. The storage modulus as a function of styrene content for
VE/MOA/styrene blends.
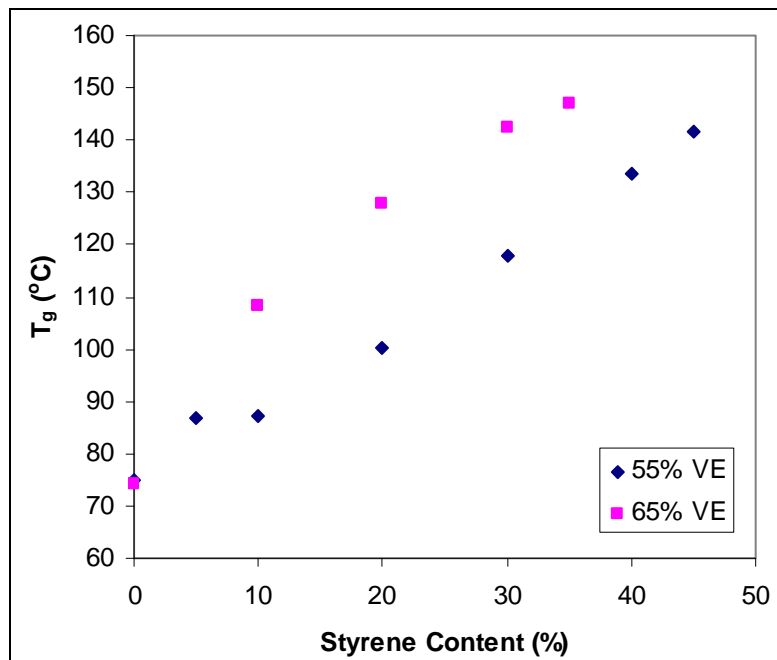
Figure 9. T_g as a function of styrene content for VE/MOA/styrene
blends.
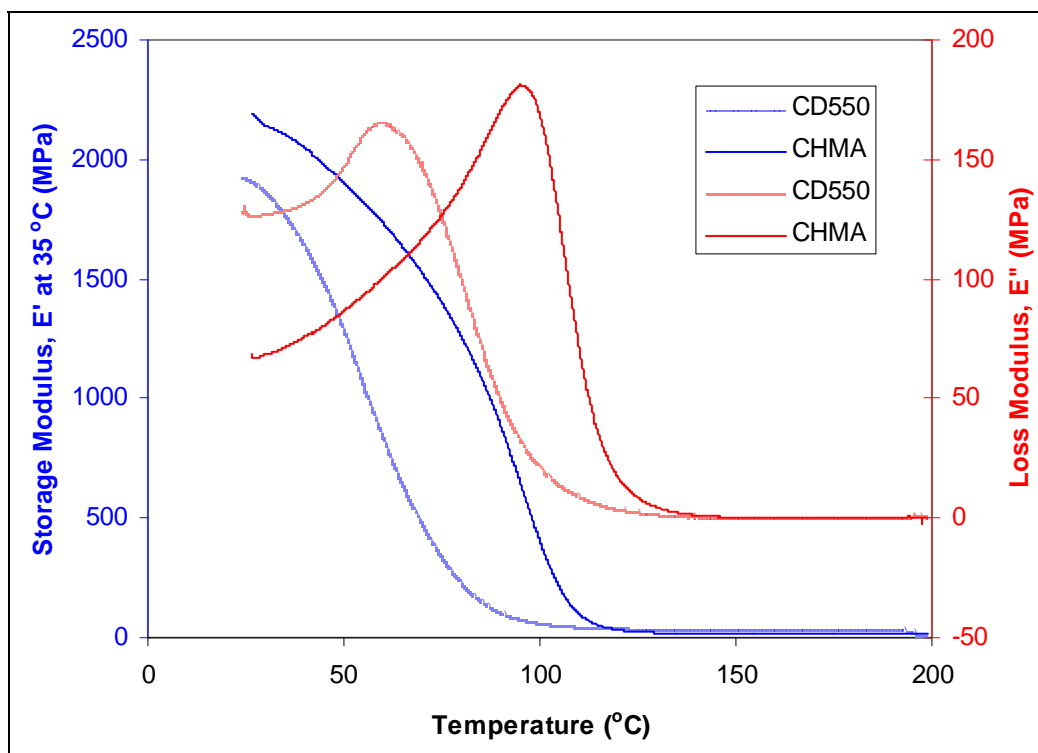
Figure 10. The storage modulus and loss modulus as a function of temperature for
VE/MLau/Styrene/CHMA 55/15/15/15 and VE/MLau/Styrene/CD-550.

Figures 11 and 12 compare the modulus, molecular weight between cross-links, and T_g of
quaternary blends of VE/MLau/styrene/non-HAP petroleum reactive diluents 55/15/15/15 to
fatty acid vinyl ester ternary resins VE/MLau/Styrene 55/15/30 and 55/30/15. These results and
other analogous formulations are tabulated in table 4. These results and comparison to the two
ternary blends allows determination of whether using petroleum reactive diluent is useful in
reducing the styrene content or reducing the MLau content in terms of dynamic mechanical
properties. The results clearly show that the using CD-550 to replace either MLau or styrene
reduced T_g and modulus. This occurred because CD-550 has a very high molecular weight and
thus had a high molecular weight between cross-links, resulting in a lower T_g. On the other
hand, using CHMA to replace the MLau content increased T_g, but using CHMA to replace
styrene caused a slight drop in the T_g. This is expected because CHMA is very similar to styrene
in molecular weight and structure. The slightly reduced properties are likely due to higher
flexibility of the methacrylate group relative to the styrene vinyl group. CD-612 caused a drop
in T_g and modulus relative to both styrene and MLau as reactive diluents. This is expected
because CD-612 is a methacryl polyethylene glycol (PEG), and PEG groups are among the most
flexible and lowest T_g chemical groups (*20*).

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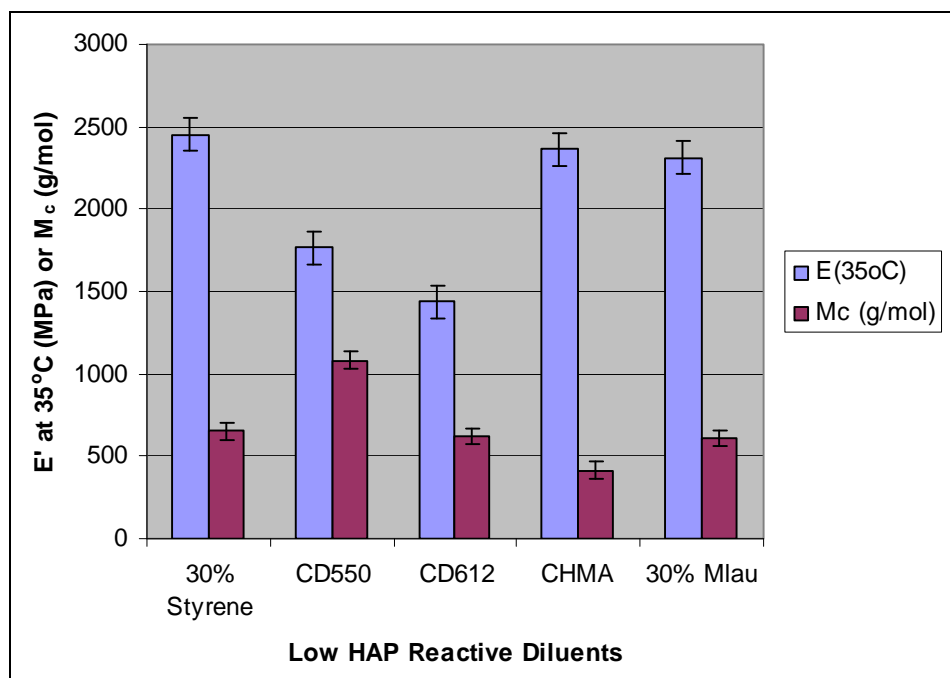
Figure 11. Storage modulus and molecular weight between cross-links as a function of mono-functional monomers for resins with 55% CN151, 15% MLau, 15% low VOC petroleum monomer, and 15% styrene compared to ternary blends with 55/15/30 and 55/30/15 CN151/MLau/Sty.
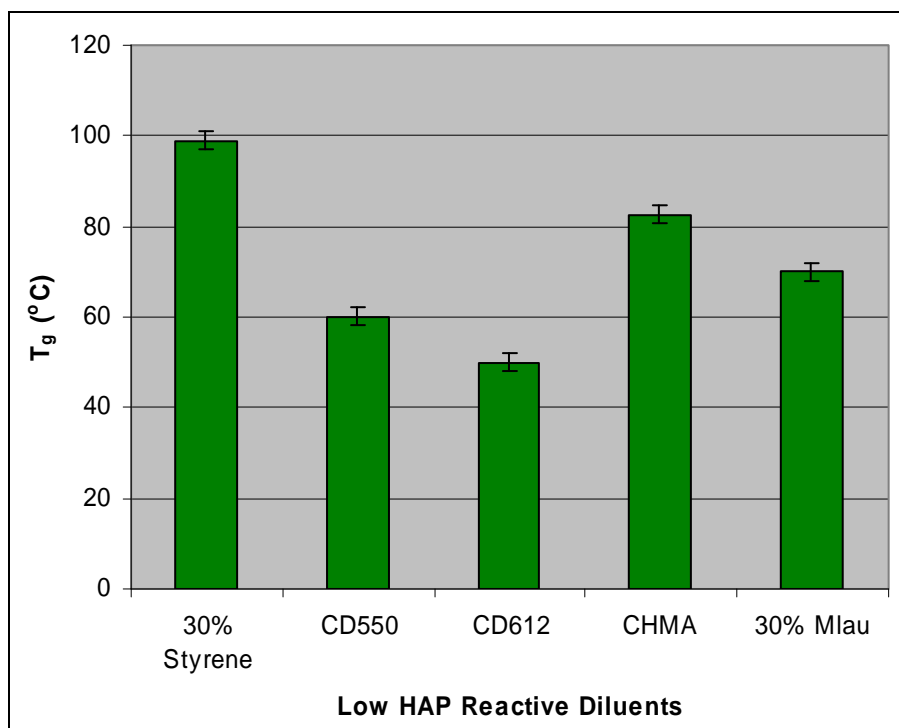
Figure 12. T_g as a function of low HAP mono-functional monomers for resins with 55% CN151, 15% MLau, 15% low VOC petroleum monomer, and 15% styrene compared to ternary blends with 55/15/30 and 55/30/15 CN151/MLau/Sty.

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Table 4. DMA properties of mono-functional low HAP petroleum reactive diluent formulations. Yellow shading indicates a property increase when replacing MLau with the low HAP petroleum monomer, but a property decrease when replacing styrene. Red indicates a property decrease when replacing either MLau or styrene.

Petroleum Monomer	Petroleum (Weight-Percent)	CN151 (Weight-Percent)	MLau (Weight-Percent)	Styrene (Weight-Percent)	E(35 °C) (GPa)	T_g (°C)	M_c (g/mol)
—	—	65	10	25	2.5	113	410
—	—	65	15	20	2.5	105	430
—	—	65	25	10	2.5	85	450
CD550	10	65	10	15	2.0	85	800
CD612	10	65	10	15	1.6	75	690
CHMA	10	65	10	15	2.5	103	530
CHMA	10	65	15	10	2.4	95	470
—	—	55	15	30	2.5	99	650
—	—	55	30	15	2.3	70	610
CD550	15	55	15	15	1.8	60	1080
CD612	15	55	15	15	2.0	50	620
CHMA	15	55	15	15	2.4	83	410

Figures 13 and 14 and table 5 show the effect of using di-functional cross-linkers to replace styrene or MLau in fatty acid vinyl ester ternary blends. Using SR239 increased the cross-link density and also improved T_g. Despite its aliphatic character, the overall short chain length of SR239 allows for higher performance relative to MLau alone as a styrene replacement, and can be used to help reduce styrene content in VE resins. Furthermore, SR239 effectively replaced up to 20 weight-percent VE without much of a reduction in T_g (table 5). However, the modulus at 35 °C reduced noticeably at 20 weight-percent SR239 because of the lower rigidity of the SR239 relative to CN151. Using SR252 as a cross-linker reduced the polymer properties and was not effective for improving performance of FAVE resins. On the other hand, SR259 was more effective than MLau in maintaining Tg while reducing styrene content through increasing the cross-link density. SR252 and SR259 are essentially the same molecule (PEG cross-linkers) except that SR252 is a dimethacrylate and has a molecular weight of ~770 g/mol while SR259 is a diacrylate and has a molecular weight of ~302 g/mol. MLau has a molecular weight of ~342 g/mol, but is mono-functional resulting in a slightly lower T_g than SR259 formulations. However, both PEG acrylates resulted in broader T_g with relatively more softening occurring at 35 °C, thus, a lower 35 °C modulus because of the molecular structure of the highly flexible chemical structure of the PEG acrylates and the higher cross-linker content vs. the ternary blends. SR480 behaved similarly relative to SR259. We expected higher performance of the SR480 because of its aromatic character and similar structure relative to a high T_g VE. However, because of the ethoxylation, the T_g of homopolymerized SR480 is –1 °C as opposed to polymerized VE, which has a T_g of ~180 °C.
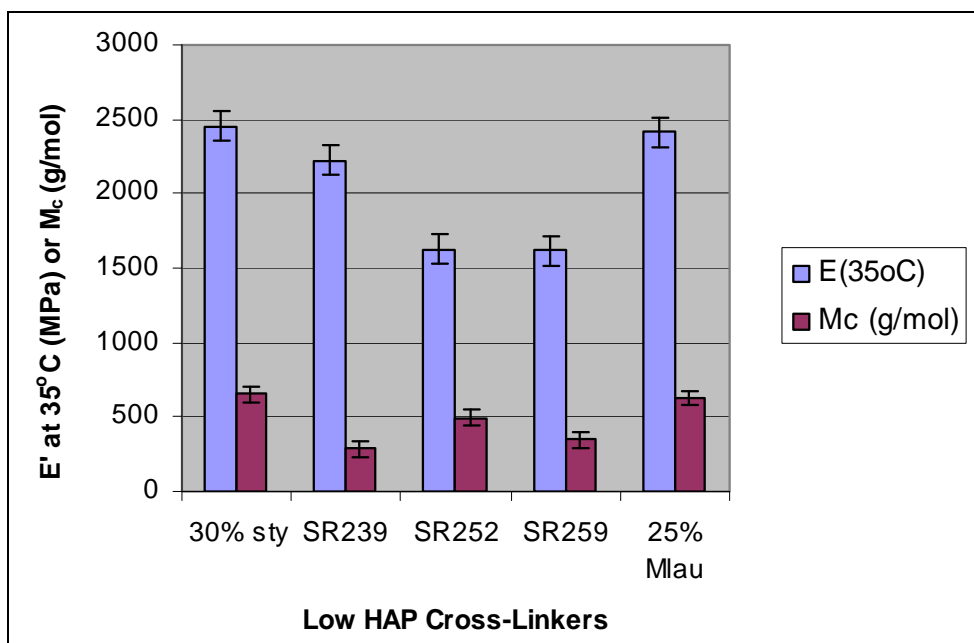
Figure 13. Modulus as a function of low VOC di-functional monomer for resins
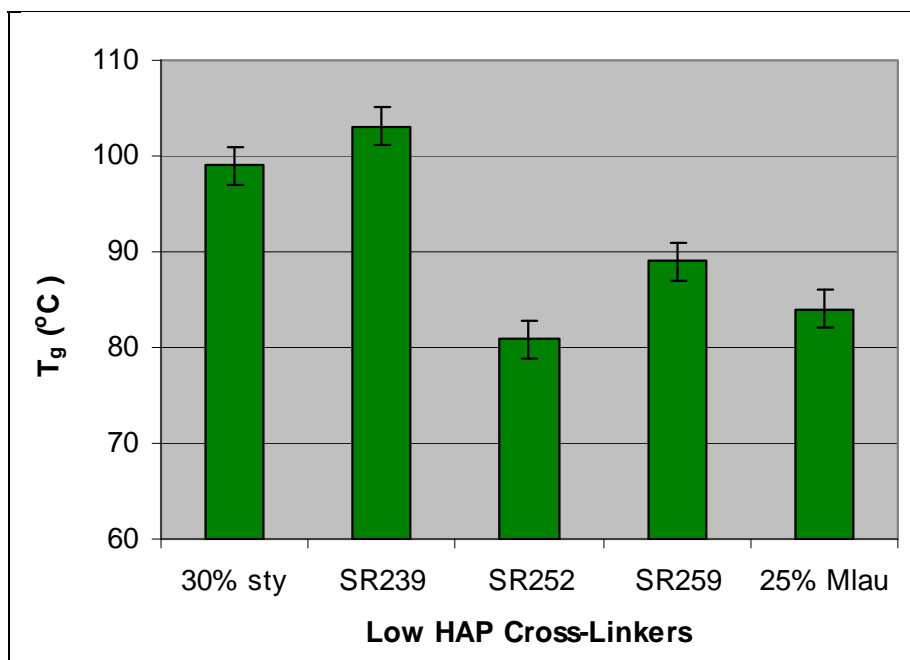containing 55% CN151, 15% MLau, 10% low VOC petroleum monomer, and
20% styrene.

Figure 14. T_g as a function of resin formulation for low VOC di-functional
monomers containing 55% CN151, 15% MLau, 10% low VOC
petroleum monomer, and 20% styrene.

Table 5. DMA properties of di-functional low VOC petroleum monomer formulations. Green shading indicates property increase when replacing styrene with the low HAP petroleum monomer. Yellow shading indicates a property increase when replacing MLau with the low HAP petroleum monomer, but a property decrease when replacing styrene. Red indicates a property decrease when replacing either MLau or styrene.

Petroleum Monomer	Petroleum (Weight-Percent)	CN151 (Weight-Percent)	MLau (Weight-Percent)	Styrene (Weight-Percent)	E (35 °C) (GPa)	T_g (°C)	M_c (g/mol)
—	—	55	15	30	2.5	99	650
—	—	55	25	20	2.4	84	630
SR239	10	55	15	20	2.2	103	290
SR252	10	55	15	20	1.6	81	500
SR259	10	55	15	20	1.6	89	350
—	—	45	15	40	2.4	94	980
—	—	45	35	20	1.9	59	850
SR239	20	45	15	20	1.8	102	250
SR252	20	45	15	20	1.4	70	340
SR480	20	45	15	20	1.6	79	380

Reviewing all of the data, it was found that the di-functional monomers produced resins with lower viscosities, higher modulus, and higher T_g than the mono-functional monomers. Because CN151/Mlau/SR239/Sty 55/15/10/20 had the lowest viscosity, 113 cP, the highest modulus, 2226 MP, and the highest T_g,103°C, SR239 was the best petroleum monomer to replace styrene content without being an HAP or VOC.

3.2.3 Glass Transition Temperature Prediction

A number of simple models exist to predict the T_g of polymer mixtures. The Fox equation (*21*) uses the mass fractions of the components, w_x, and the T_g of the pure components (table 1), T_{gx}, to calculate the glass transition temperature:

$$T_g = \left(\sum_{n=i} \frac{W_i}{T_{gi}} \right)^{-1}.$$
(2)

To determine if T_g of these blends of VE, MFA, and styrene can be predicted using the Fox equation, T_g of the pure components were measured. T_g of pure styrene is well known to be 100 °C. Pure VE 828 was cured using 0.5 weight-percent trigonox and found to have a T_g of 180 °C. Pure MLau was also polymerized and found to have a T_g of –30 °C (*11*, *22*). Resins with various contents of VE 828, MLau, and styrene were prepared and cured, and their T_g were measured using DMA. Figure 15 shows that the experimentally measured T_g at 2 °C/min ramp rates very closely matched the predictions from the Fox equation. Therefore, the Fox equation can be used to predict T_g of these binary and ternary blends of monomers. Furthermore, because T_g of MLau is so low, the Fox equation shows that improved overall T_g can be best achieved by increasing T_g of the fatty acid component. A simple way to do this would be to use shorter chain fatty acids, such as hexanoic acid instead of lauric acid (*10*, *11*).
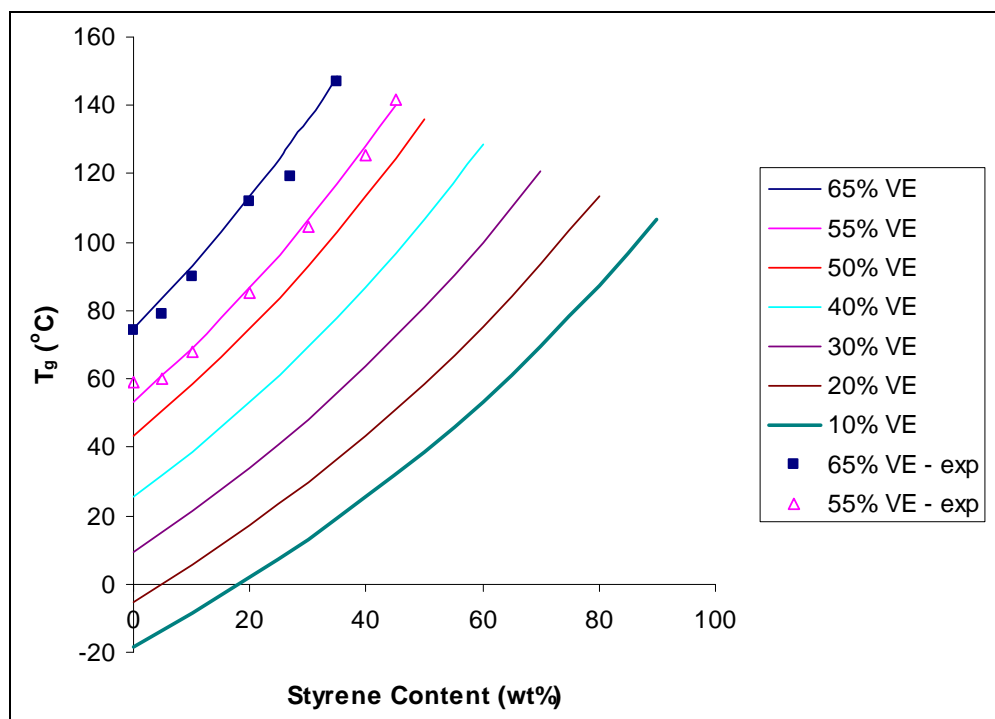
Figure 15. The Fox equation can be used to predict T_g of blends of VE, MLau, and styrene.

The Fox equation (equation 2) was used to predict the T_g of the non-HAP petroleum monomer component by rearranging the equation to:

$$T_{g1} = W_1 \left(\frac{1}{T_g} \sum_{n=i+1} \frac{W_i}{T_{gi}} \right)^{-1}.$$

(3)

The predicted monomer T_g's are listed in table 6. Overall, the standard deviation in the predicted monomer T_g from formulation to formulation is low, except for SR-252. For the monomers with the known homopolymer T_g, the percent error was 0.6% for CD-550 and 13.4% for SR-480. Overall, the error was low and indicates that the Fox equation is a useful method for predicting the T_g of vinyl ester resin blends.

Table 6. Fox equation predictions of the homopolymer Tg of the non-HAP petroleum monomers.

Monomer	Formulation (VE/MLau/Sty/Petroleum Monomer)					Average T_g (°C)	Std. Dev. (°C)
	65/10/15/10	65/15/10/10	55/15/15/15	55/15/20/10	45/15/20/20		
CHMA	17.1	29.2	15.8	—	—	20.7	7.4
CD550	–64.0	—	–62.7	—	—	–63.4	0.9
CD612	–94.0	—	–87.0	—	—	–90.5	5.0
SR239	—	—	—	150.9	149.0	150.0	1.4
SR259	—	—	—	22.2	—	22.2	—
SR252	—	—	—	–23.7	3.7	–10.0	19.4
SR480	—	—	—	35.6	—	35.6	—

4. Conclusions

Mono- and di-functional non-HAP petroleum monomers were blended into fatty acid vinyl ester resins in an effort to decrease styrene content, reduce viscosity, and improve polymer properties. It was found that CHMA was the most effective reactive diluent in replacing MLau because it effectively reduced viscosity and improved thermal and mechanical properties. However, replacing styrene with CHMA resulted in both a viscosity increase and polymer property decrease. CD612 resulted in high resin viscosities and lower polymer properties, while using CD550 to replace some MLau reduced the resin viscosity but also reduced polymer properties. All petroleum di-functional monomers were effective in reducing the viscosity through replacement of the MLau fraction. However, only HDDMA allowed for further reduction in styrene content with little effect on viscosity and improved or similar polymer properties. Ignoring economics, the use of a small percent HDDMA to replace styrene or MLau is optimum and would result in improved resin and polymer performance. CHMA can be used to effectively reduce the MLau content in the formulations with improved resin and polymer performance, but would not allow for further reduction in styrene content. All of the other monomers investigated can result in some property improvements, but simultaneously result in other property reduction.

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List of Symbols, Abbreviations, and Acronyms

CD550   Methoxy PEG 350 methacrylate

CD612   Ethoxy (4) nonyl phenol methacrylate

CHMA   Cyclohexylmethacrylate

CN151   Sartomer vinyl ester

DLSME   Defense Land Systems for Miscellaneous Equipment

DMA   Dynamic mechanical analysis (polymer thermomechanical analysis)

E'   Storage modulus

E''   Loss modulus

EPA   Environmental Protection Agency

FA   Fatty acid

FAVE   Fatty acid vinyl ester

FG   Fiber glass

GM   Glycidyl methacrylate

HAP   Hazardous air pollutant

HDDMA   1,6-hexanediol dimethacrylate

MFA   Methacrylate fatty acid

MLau   Methacrylate lauric acid

MOct   Methacrylate octanoic acid

NESHAP   National Emissions Standards for Hazardous Air Pollutants

SR239   1,6-hexanediol dimethacrylate

SR252   PEG 600 dimethacrylate

SR259   PEG 200 diacrylate

SR480   Ethoxylated (10) bisphenol A dimethacrylate

Sty   Styrene

tan(δ)	Ratio of loss modulus to storage modulus
T_g	Glass transition temperature of polymer
TGA	Thermogravimetric analysis
UPE	Unsaturated polyester
VE	Vinyl ester

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